

| L Number | Hits | Search Text  | DB                               | Time stamp       |
|----------|------|--|----------------------------------|------------------|
| 1        | 1466 | (etching or removing) with molybdenum  | USPAT;<br>US-PGPUB               | 2003/02/08 15:55 |
| 2        | 320  | ((etching or removing) with molybdenum)<br>and etchant   | USPAT;<br>US-PGPUB               | 2003/02/08 15:34 |
| 3        | 310  | ((etching or removing) with molybdenum)<br>and etchant) and (substrate or<br>semiconductor)  | USPAT;<br>US-PGPUB               | 2003/02/08 15:36 |
| 4        | 260  | ((etching or removing) with molybdenum)<br>and etchant) and (substrate or<br>semiconductor)) and @ad<=20000320   | USPAT;<br>US-PGPUB               | 2003/02/08 15:55 |
| 6        | 43   | ((etching or removing) with molybdenum)<br>and etchant) and (substrate or<br>semiconductor)) and @ad<=20000320) and<br>(molybdenum with (peroxide or water))   | USPAT;<br>US-PGPUB               | 2003/02/08 15:42 |
| 7        | 1290 | ((etching or removing) with molybdenum)<br>and @ad<=20000320   | USPAT;<br>US-PGPUB               | 2003/02/08 16:01 |
| 8        | 252  | ((etching or removing or etchant) with<br>molybdenum) same (peroxide or water or<br>(ammonium adj sulfate) or (ammonium adj<br>nitrate) or (sodium adj dihydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>phosphate) or (trisodium adj citrate) or<br>(ammonium adj acertate))  | USPAT;<br>US-PGPUB               | 2003/02/08 16:23 |
| 9        | 229  | ((etching or removing or etchant) with<br>molybdenum) same (peroxide or water or<br>(ammonium adj sulfate) or (ammonium adj<br>nitrate) or (sodium adj dihydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>phosphate) or (trisodium adj citrate) or<br>(ammonium adj acertate))) and<br>@ad<=20000320  | USPAT;<br>US-PGPUB               | 2003/02/08 16:01 |
| 10       | 191  | ((etching or removing or etchant) with<br>molybdenum) same (peroxide or water or<br>(ammonium adj sulfate) or (ammonium adj<br>nitrate) or (sodium adj dihydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>phosphate) or (trisodium adj citrate) or<br>(ammonium adj acertate))) and<br>@ad<=20000320) not (((((etching or<br>removing) with molybdenum) and etchant)<br>and (substrate or semiconductor)) and<br>@ad<=20000320) and (molybdenum with<br>(peroxide or water))) | USPAT;<br>US-PGPUB               | 2003/02/08 16:02 |
| 11       | 102  | ((etching or removing or etchant) with<br>molybdenum) same (peroxide or water or<br>(ammonium adj sulfate) or (ammonium adj<br>nitrate) or (sodium adj dihydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>citrate) or (disodium adj hydrogen adj<br>phosphate) or (trisodium adj citrate) or<br>(ammonium adj acertate))  | EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/02/08 16:23 |

US-PAT-NO: 6127908

DOCUMENT-IDENTIFIER: US 6127908 A

TITLE: Microelectro-mechanical system actuator device and  
reconfigurable  
circuits utilizing same

----- KWIC -----

The next step is to cut the wafer into individual chips.  
The chips are then  
placed in a release system where movable electrodes are  
then released from the  
substrate by etching away the molybdenum as shown in FIG.  
6H. The etching of  
the molybdenum can be done with hydrogen peroxide, which is  
rinsed with water,  
acetone, and then cyclohexane in the release system. The  
chips in the system  
are then cooled to -10.degree. C., to freeze the  
cyclohexane and purged with  
nitrogen at low pressure to evaporate away the cyclohexane.  
The moveable  
electrode 624 is now curled up away from the substrate.  
The chips are now  
ready for testing, packaging and operation.

US 5513131

DERWENT-ACC-NO: 1996-258739  
DERWENT-WEEK: 199626  
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TITLE: Molybdenum etching process - using etchant of  
ferric sulphate or  
ferric-ammonium sulphate, and then rinsing the article in  
water

INVENTOR: CHEN, H H; DAVID, L D ; HARRIS, D B

PATENT-ASSIGNEE: INT BUSINESS MACHINES CORP[IBMC]

PRIORITY-DATA: 1994US-0250896 (July 7, 1994)

PATENT-FAMILY:

| PUB-NO       | PUB-DATE     | LANGUAGE |
|--------------|--------------|----------|
| PAGES        | MAIN-IPC     |          |
| US 5518131 A | May 21, 1996 | N/A      |
| 005          | C01G 039/00  |          |

APPLICATION-DATA:

| PUB-NO       | APPL-DESCRIPTOR | APPL-NO        |
|--------------|-----------------|----------------|
| APPL-DATE    |                 |                |
| US 5518131A  | N/A             | 1994US-0250896 |
| July 7, 1994 |                 |                |

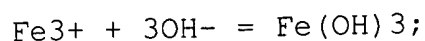
INT-CL (IPC): C01G039/00

ABSTRACTED-PUB-NO: US 5518131A

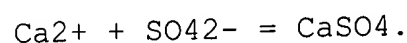
BASIC-ABSTRACT: A method of etching molybdenum comprises:

(a) providing a  
molybdenum article to be etched with a resistive coating  
covering all but  
desired feature areas, where the feature areas do not have  
a resistive coating  
and are exposed for etching; (b) etching the feature areas  
of the molybdenum  
article with an etching selected from ferric sulphate and  
ferric ammonium  
sulphate, the etching being performed at ambient pressure;  
and (c) rinsing the  
molybdenum article with water after etching.

The method of etching molybdenum with reduced treatment waste comprises: (a), (b) and (c) as above, followed by: (d) collecting a rinse produced during the rinsing step; (e) pptn. of iron from the rinse by raising the pH of the rinse above 2



and (f) pptn. of sulphate from the rinse by addition of lime



No poisonous or corrosive residues can thus pass an ordinary waste treatment facility.

The etching step is performed by spraying the etchant on the feature areas, or by immersing the article in the etchant.

USE - The process is used for etching molybdenum for making a metal mask to be used in electronic packaging and semiconductor fabrication.

ADVANTAGE - The process reduces hazardous treatment waste. The etchant does not contain cyanide and so does not emit noxious fumes when heated.

CHOSEN-DRAWING: Dwg.0/2

TITLE-TERMS:

MOLYBDENUM@ ETCH PROCESS ETCH FERRIC SULPHATE FERRIC  
AMMONIUM SULPHATE RINSE  
ARTICLE WATER

DERWENT-CLASS: E31 L03 M14 U11

CPI-CODES: E32-A04; E34-D02; E35-Q; E35-U03; E35-U04;  
L04-C05; M14-A03;

EPI-CODES: U11-C07B; U11-C07C2; U11-D03;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

A426 A940 C108 C316 C500 C540 C730 C801 C803 C804  
C805 C806 C807 M411 M782 M903 M904 Q454 Q463

Markush Compounds

199626-C2701-M

Chemical Indexing M3 \*02\*

Fragmentation Code

A426 A940 C108 C316 C540 C730 C801 C802 C803 C804  
C805 M411 M782 M903 M904 M910 Q454 Q463

Specific Compounds

01729M

Registry Numbers

1729U

Chemical Indexing M3 \*03\*

Fragmentation Code

A426 A940 C101 C108 C550 C730 C801 C802 C804 C805  
C807 M411 M720 M903 M904 M910 N421 N513 Q454 Q463

Specific Compounds

01507P

Registry Numbers

1507P

Chemical Indexing M3 \*04\*

Fragmentation Code

A220 A940 C108 C316 C540 C730 C801 C802 C803 C804  
C805 M411 M720 M903 M904 M910 N421 N513 Q454 Q463

Specific Compounds

01767P

Registry Numbers

1767P

UNLINKED-DERWENT-REGISTRY-NUMBERS: 1507P; 1729U ; 1767P

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1996-081842

Non-CPI Secondary Accession Numbers: N1996-217742

US-PAT-NO: 5547896

DOCUMENT-IDENTIFIER: US 5547896 A

TITLE: Direct etch for thin film resistor using a hard mask

----- KWIC -----

2. The method of claim 1 where the thin film resistor material comprises NiCr and wherein the hard mask comprises one of TiW and molybdenum and the first etchant comprises hydrogen peroxide.

4. The method of claim 1 where the thin film resistor material comprises CrSi and wherein the hard mask comprises one of TiW and molybdenum and the first etchant comprises hydrogen peroxide.

17. The method of claim 16 where the thin film resistor material comprises NiCr and wherein the hard mask comprises one of TiW and molybdenum and the first etchant comprises hydrogen peroxide.

19. The method of claim 16 where the thin film resistor material comprises CrSi and wherein the hard mask comprises one of TiW and molybdenum and the first etchant comprises hydrogen peroxide.

US-PAT-NO: 4470873

DOCUMENT-IDENTIFIER: US 4470873 A

TITLE: Method of manufacturing magnetic sensor comprising at least two magnetoresistive elements

----- KWIC -----

Next, as depicted in FIG. 7, an electrically insulating photoresistive film 9 of negative type was applied on the second MR film 4, and then an opening 9a was formed in the photoresist film 9 at a bottom of the through-hole 8. At the same time an opening 9b was formed in the photoresist film 9 at a portion corresponding to the junction to the second MR film 4. In this manner, the first and second MR films 2 and 4 were partially exposed. The insulating photoresist film 9 was made of polyimide which has a superior electrical insulating property. Next, without removing the insulating photoresist film 9, a metal film 10 made of double layer of molybdenum (Mo) and gold (Au) was deposited as shown in FIG. 10. The vapour deposition of the metal film 10 was effected in such a manner that the Mo and Au layers have thicknesses of 2,000 .ANG. and 5,000 .ANG., respectively, while the substrate 1 was heated to a temperature of 250.degree. C. Then after applying a photoresist film of positive type on the metal film 10, the metal film was selectively etched by means of a photomask 11 shown in FIG. 9 to obtain a desired pattern of conductor. During the etching, ceric ammonium nitrate etchant was used for the molybdenum layer and a potassium iodide etchant was use for

etching the gold layer. Finally the photoresist film remained on the metal pattern was removed to obtain the magnetic sensor illustrated in FIG. 10.



US-PAT-NO: 4301233

DOCUMENT-IDENTIFIER: US 4301233 A

TITLE: Beam lead Schottky barrier diode for operation at millimeter and submillimeter wave frequencies

----- KWIC -----

In step 14, the device is submerged in a 30 percent aqueous solution of hydrogen peroxide to etch through the molybdenum layer. Note that the undercutting of the molybdenum layer in step eight causes the first gold layer 605 and the metallic layers above to act as a mask for the molybdenum, preventing the passivation layers from covering the molybdenum layer. By this process, the molybdenum layer is left exposed to the etching effect of the hydrogen peroxide and the molybdenum, as well as all the layers above it are removed leaving the structure shown in FIG. 6N. Note in this Figure, two additional layers within the gallium arsenide substrate are revealed. The first is a conducting layer 608 referred to as the N+layer. This layer is located directly beneath the N layer. The second is the semi-insulating layer 613 located directly beneath the N+layer.

US-PAT-NO: 4067100

DOCUMENT-IDENTIFIER: US 4067100 A

TITLE: Method of making a semiconductor device

----- KWIC -----

After the passivation layer has been etched as illustrated in FIG. 6, the metal layer is removed by the following methods. The method for removing aluminum or molybdenum are as follows. For aluminum, hot phosphoric acid, hydrochloric acid or aqua regia are used. For removing molybdenum, a solution of ceric ammonium nitrate which has the form of  $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{O}$  including a small amount of nitric acid  $\text{HNO}_3$  is used. A second method for removing the double layer of chromium and gold or platinum is as follows. The gold or platinum layer is etched by aqua regia and then the chromium layer is etched by a mixed solution of ceric ammonium nitrate and perchloric acid.

US-PAT-NO: 4551908

DOCUMENT-IDENTIFIER: US 4551908 A

TITLE: Process of forming electrodes and interconnections  
on silicon  
semiconductor devices

----- KWIC -----

Then, the molybdenum film is annealed in a hydrogen gas atmosphere at a temperature of 500 degrees Celsius for 20 minutes to form a layer of a molybdenum silicide self-aligned with the direct contact hole. Such a low-temperature annealing process is necessary to self-align the molybdenum silicide layer with the direct contact hole, that is, with a region in which the molybdenum film is in contact with the silicon substrate. The annealing should be carried out in a non-reducing atmosphere for a few tens of minutes in a temperature range of from 400 degrees Celsius, at which the silicide starts being formed, up to about 650 degrees Celsius. If the molybdenum film were annealed at a high temperature of about 800 degrees Celsius or more, the silicide would tend to grow out of the direct contact hole onto the gate oxide layer 303, thus failing to meet the requirement that the molybdenum silicide layer be self-aligned with the direct contact hole. Thereafter, a hydrogen peroxide solution is applied to selectively remove an unreacted film of molybdenum, as shown in FIG. 3e, whereupon molybdenum silicide layer 309 and the n.sup.+ -doped layer 308 which acts as a source or drain depending on a circuit design, are formed in the direct contact hole 305

is self-alignment.

The molybdenum silicide layer 309 thus formed is of hexagonal  $\text{MoSi}_2$  as determined by an X-ray diffraction analysis. Then, the molybdenum silicide layer 309 is annealed in a nitrogen gas atmosphere for 40 minutes at a temperature of 1,000 degrees Celsius in order to make the arsenic-implanted n.s.p. layer 308 electrically active and molybdenum silicide layer 309 less resistant. The hexagonal molybdenum silicide layer 309 is converted by such a high-temperature annealing process into tetragonal  $\text{MoSi}_2$  of a high-temperature phase. The inventors have found as a result of various experiments that the high-temperature annealing should be effected in a non-reducing atmosphere to maintain the uniformity and flatness of the silicide formed by the low-temperature annealing after the high-temperature annealing process has been effected. If the molybdenum silicide layer were annealed in a reducing atmosphere as of a hydrogen gas at a temperature of 800 degrees Celsius or more, the uniformity and flatness of the molybdenum silicide layer would be rendered extremely poor, resulting in a failure of such a process to find application in device fabrication. It has been found that the molybdenum silicide layer can be annealed in a non-reducing atmosphere such as a nitrogen gas without losing the uniformity and flatness the silicide layer has.

According to a third embodiment as shown in FIGS. 5a through 5g, a silicide of molybdenum is formed on a gate of an interconnection of polycrystalline silicon and on the surface of impurity-doped layers in source and drain regions. As shown in FIG. 5a, field oxide films 12 are formed on a p-type silicon substrate 11 by ordinary selective oxidation process. Then, a gate

oxide film 13 having a thickness of 300 .ANG. is formed on the silicon substrate 11 by way of thermal oxidation. As illustrated in FIG. 5b, a film of polycrystalline silicon which is 3,000 .ANG. thick and contains phosphorus as a dopant is deposited and patterned as a gate electrode 14 by a photoetching process. Then, a relatively thick film 15 of molybdenum having a thickness of 800 .ANG. is deposited by vacuum evaporation as shown in FIG. 5c. In the following step, arsenic ions in a dose of  $5 \times 10^{15} \text{ cm}^{-2}$  are implanted at an acceleration voltage 300 keV to mix an interface between the relatively thick film 15 of molybdenum and the polycrystalline silicon. Then, the structure is annealed in a hydrogen gas atmosphere for 20 minutes at a temperature of 500 degrees Celsius to cause a silicide forming reaction at the mixed interface. Subsequently, unreacted residuals of molybdenum on the oxidized-silicon film are selectively removed by an etchant of hydrogen peroxide, whereupon, as shown in FIG. 5d, a layer 16 of molybdenum silicide having a thickness of 2,000 .ANG. is formed in self-alignment solely on the gate of polycrystalline silicon. Then, as shown in FIG. 5e, a film 17 of molybdenum which is 400 .ANG. thick is deposited by vacuum evaporation after the silicon substrate has been exposed at the source and drain regions. Arsenic ions in a dose of  $5 \times 10^{15} \text{ cm}^{-2}$  are implanted at 150 keV to mix an interface between the molybdenum film 17 and the silicon substrate 11. The construction is then annealed in a hydrogen gas atmosphere for 20 minutes at a temperature of 500 degrees Celsius, and thereafter, is treated with an etchant of hydrogen peroxide. As a result, layers 18 of molybdenum silicide which are 1,000 .ANG. thick are formed in

self-alignment with the source and drain regions, and n-type high-density impurity-doped layers 19 are formed in self-alignment beneath the molybdenum silicide layers 18, respectively, as illustrated in FIG. 5f. The structure is now annealed in a nitrogen gas atmosphere for 20 minutes at a temperature of 950 degrees Celsius for thereby rendering the two layers of molybdenum silicide less resistive and activating the n-type impurity layers. Then, as shown in FIG. 5g, an interlayer insulating film 20 as of oxidized silicon is deposited, contact holes are defined in the film 20 in desired positions at the source and drain regions, and a layer 21 of aluminum which serves as an interconnection is deposited and patterned. The assembly is then annealed in a hydrogen gas atmosphere for about 30 minutes at 500 degrees Celsius to remedy electron-gun-induced damages which are caused upon vapor deposition of aluminum and during a process of electron beam lithography.

There is thus fabricated a MOS field-effect transistor in which the gate of polycrystalline silicon and the source and drain regions are covered at their surfaces with the layers of molybdenum silicide. According to the present embodiment, for a molybdenum silicide of 2000 .ANG., a low resistance gate wiring could be realized having a sheet resistivity of 6 to 7 .OMEGA./square, and for a molybdenum silicide of 1000 .ANG., a low resistance source/drain layer could be realized having a sheet resistivity of 13 to 14 .OMEGA./square. The above sheet resistivity is much smaller than 30-100 .OMEGA./square of source and drain impurity layers in a semiconductor device produced by a conventional fabrication process including arsenic ion implantation and activation by way of annealing in an electric furnace.

According to the present embodiment, the series of steps of vacuum evaporation of molybdenum, ion implantation, annealing in a hydrogen gas for 20 minutes at 500 degrees Celsius, and etching away unreacted molybdenum films is carried out twice to form different thicknesses of molybdenum layers on the gate of polycrystalline silicon and the source and drain regions. Where the sheet resistivities may be equal to each other, the above series of steps can be carried out only once. While in the illustrated embodiment, the layers of molybdenum silicide are formed on both the gate of polycrystalline silicon and the source and drain regions, the layer of molybdenum silicide may be formed on either the gate of polycrystalline silicon or the source and drain regions. Since the molybdenum silicide layer which is uniform and has much fewer grain boundaries serves as a barrier metal in the contact of an aluminum/molybdenum silicide/n.sup.+ -Si construction, no aluminum alloy spikes would be caused during annealing in a hydrogen gas atmosphere at 500 degrees Celsius, a temperature which is sufficiently high to remedy electron-gun-induced damages.

selectively etching away an unreacted layer of said molybdenum on said insulating film so as to self-align the silicide layer of molybdenum with said opening; and

thereafter etching away an unreacted layer of molybdenum on said insulating films to form a layer of molybdenum silicide selectively on said exposed portion of said silicon substrate;

thereafter etching away an unreacted layer of molybdenum to form a layer of molybdenum silicide selectively on said exposed impurity-doped layer;

annealing the structure at a temperature of 400 to 650 degrees Celsius so as to cause siliciding of the layer of molybdenum only at said interfaces, and then selectively etching away an unreacted portion of said layer thereby forming a layer of a molybdenum silicide in self-alignment with the portions of said surface of said silicon substrate for forming said source and drain regions and for forming with said patterned silicon film said gate electrode wiring; and



DT 2425379 A1

DERWENT-ACC-NO: 1975-22761W  
DERWENT-WEEK: 197514  
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TITLE: Accurately etching molybdenum with water and  
hydrogen peroxide - for  
mfr. of integrated and thin film-circuits, and photomasks

PATENT-ASSIGNEE: WESTERN DIGITAL CORP[WDIGN]

PRIORITY-DATA: 1973US-0391635 (August 27, 1973)

PATENT-FAMILY:

| PUB-NO        | PUB-DATE       | LANGUAGE |
|---------------|----------------|----------|
| PAGES         | MAIN-IPC       |          |
| DE 2425379 A  | March 27, 1975 | N/A      |
| 000           | N/A            |          |
| JP 50045742 A | April 24, 1975 | N/A      |
| 000           | N/A            |          |

INT-CL (IPC): C23F001/00

ABSTRACTED-PUB-NO: DE 2425379A  
BASIC-ABSTRACT: A soln. of H2O and H2O2 is used to etc Mo.  
The pref. etchant  
contains a wetting agent, esp. a detergent, and the pref.  
ratio of H2O:H2O2 is  
1-4 to 3:2. A Mo photomask is pref. made by depositing a  
layer of Mo on a  
transparent substrate and a phot-lacquer is used to expore  
the Mo regions to be  
dissolved. Provides a non-poisonous etchant making highly  
accurate masks  
without attacking the photo-lacquer.

TITLE-TERMS:

ACCURACY ETCH MOLYBDENUM WATER HYDROGEN PEROXIDE  
MANUFACTURE INTEGRATE THIN  
FILM CIRCUIT PHOTOMASK

DERWENT-CLASS: M14

CPI-CODES: M14-A;